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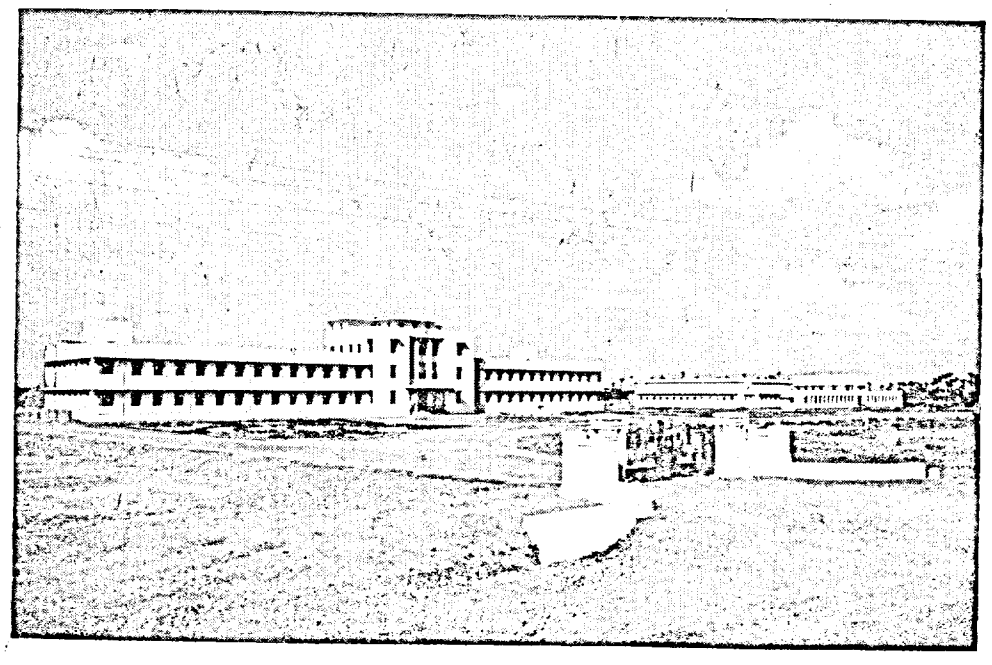

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Bulletin of the

Central Leather Research Institute

MADRAS

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PHYSICAL AND CHEMICAL CHARACTERISTICS OF SOME INDIAN LEATHERS - PART III

INDIAN CHAMOIS LEATHERS

Y. NAYUDAMMA, T. S. RANGANATHAN & B. M. DAS.

SUMMARY

India produces a good amount of chamois leathers from goat skins. Very little data is available on the chemical and physical properties of the leathers so produced. At the instance of Indian Standards Institution, a number of chamois leathers manufactured in India were collected and analysed. The ranges for chemical and physical characteristics are found to be moisture 15-20%, hide substance 65-75%, water sols. less than 4%, free fat 5-10%, bound fat 1-5%, insol. ash 2-6%, total ash 2-5%, HCHO Nil-1% pH of water sols. 6-8, Water absorption: Q½ hr. 200-325, Q24 hr. 250-400, Sink test 10 sec. 2 min. Filter test (B.O.C.) 1 min.-5 min.

In India, chamois leather is generally made from rejection quality spready goat skins. The total annual production of goat skins in India is estimated at 25 million skins of which 15 million skins are exported mostly to U.S.A., fetching an annual income of 5.5 crores of rupees. About 10 million skins are estimated to go into production of East Indian tanned leathers. Thus the market for good quality goat skins is competitive and only the rejection quality skins are taken up for chamois leather manufacture. Sheep splits are generally used for the manufacture of chamois leathers in Western countries but such is not the case in India. The organised tanneries that produce chamois leather in India are hardly 6, in number.

In India, chamois leather is mainly used for cleaning motor cars principally to a small extent for cleaning spectacles and lenses and for polishing metalwares. But with the advent of oil refineries and increased consumption of aviation fuel by the expanding net-work of airlines, a new market is being opened for this leather for petrol filtration. There is also a good demand for Indian chamois leather in foreign countries. The potentialities of developing this industry in an organised manner are thus great.

At present, chamois leather is manufactured largely by tanning goat skins with imported cod oil and to a small extent with

locally available sardine oil from the West Coast of India. The tanning is usually done by a combination formaldehyde and oil tannage.

Very little data are available on the chemical and physical properties of leathers so produced and to collect data on these properties, a number of samples from various chamois manufacturers in India were obtained and duly analysed. The results thus obtained are reported in this paper.

Experimental :

(*a*) *Chemical* : Samples for analysis were cut from the chamois leathers from the official positions prescribed for both the chemical and physical properties. Moisture, hide substance, total ash, insoluble ash, pH of water solubles and free fat contents were obtained by standard official procedures. Water solubles were determined by shaking the leather pieces with 10 times their weight of water for 18 hours and evaporating an aliquot portion of the extract. Acid soluble hide substance was determined by the method suggested by Booth and Mayer.[1] Bound grease was determined by digesting the leather, after extraction with petroleum ether, on a steam bath with 50 cc. of alcohol containing 8% sodium hydroxide, evaporating the alcohol, dissolving the residue in 50 cc. of hot water, boiling with 30 cc. of conc. hydrocloric acid, dissolving the liberated fatty acid in ether and then drying and weighing.[2] Formaldehyde was determined according to the method of Highberger and Retzch.[3]

Physical Properties

(i) *Water Absorption* : A disc of 3 cm. dia. was cut and weighed (W_1). This was soaked in 25 cc. of water at room temperature in a tared, covered dish for 30 mins. The sample was withdrawn with forceps, draining the adhering water back into the dish. (No blotting). The disc was then weighed (W_2). The disc was then put into a second dish with 25 cc. of water at room temperature. The disc was allowed to stand in this dish for 24 hours and then removed, drained and weighed as before (W_3). The solution was also evaporated and the residue weighed (R_2).

$$Q\,\tfrac{1}{2}\text{ hr.} = \%\text{ water absorption in }\tfrac{1}{2}\text{ hr.} = \frac{(W_2 + R_1 - W_1)}{W_1} \times 100$$

$$Q\,24\text{ hrs.} = \%\text{ water absorption in 24 hrs.} = \frac{(W_3 + R_1 + R_2 - W_1)}{W_1} \times 100$$

(ii) *Sink or Soaking Test* : A sample of 11 x 1 cm. was cut with a sharp knife. Water was taken in a 2 litre beaker (height of water 8″). The sample was placed in this water and the time to sink noted. The time taken to sink to the bottom of the beaker is taken as an index of the wettability of the leather.

(iii) *Petrol Filter Test* : (*a*) *B.O.C. Test* : The leather was washed with soap, and soaked overnight in petrol. Next day, a mixture of petrol and water was allowed to pass through the sample. After the last drop of petrol has passed, the interval before the first drop of water comes out should be at least 1½ mins. (B.O.C.).

(*b*) *American Federal Specification* : 5 cc. of distilled water shall be pipetted into the 25 cc. of gasolene. A piece of leather of approx. 16 sq. in. shall be wet with pure gasolene before the filtering begins. The leather shall be placed over the funnel and the 30 cc. of gasolene and water mixture shall be poured into it. The filtrate shall be collected in an absolutely dry beaker. There shall be no visible globule of water in the filtrate. A crystal of indicator can be added to the filtrate to facilitate visibility.

The leather when used as a filter for gasoline shall remove 100% of the water added to the gasoline and the filtrate shall be clear. The time required for the gasoline to pass through shall be not more than 60 sec.

Data and Discussion :

The data for 19 samples as worked out on 15% moisture basis are given in table I :

From a consideration of the table, the following observations are made.

Content	*Minimum*	*Maximum*	*Average*
Moisture	15.63	21.63	19.01
On 15% moisture			
Hide substance	59.61	75.80	69.8
Water sols	1.26	4.56	2.37
Free fat	1.40	11.20	5.065
Bound fat	1.277	5.36	2.415
Insol. ash	1.014	14.353	4.21
Total ash	2.28	14.830	5.12
HCHO	0.055	0.675	0.274
pH of water sols	6.1	9.8	7.57
Water absorption :			
$Q\frac{1}{2}$ hr.	216	348	293.4
Q24 hr.	247	379	309.0
Sink test	10 sec.	2 hrs.	55 sec.
Filter test-stands (BOC)	1 min.	8½ min.	5 min.

Physical Properties :

Sink test : The sink test depends on many factors like the extent of removal of grain from the skin, free oil present and also on the nature of opening up of the fibres. The longer time taken by the sample No. 17, may be due to the high amount of free grease present and in the case of sample 18, it may be due to the less opening up of the fibre structure. This is also evident from the water absorption figures which are very low compared to other samples. Only if the fibres are well split and opened up water absorption will be considerable. Even if a higher content of grease is present in sample 6, the quick soaking may be due to the loose nature of the fibres of the skin or it might have been achieved by incorporating a wetting agent in the leather. In the case of sample No. 1, the long time taken i.e., 2 hrs. to sink was found to be due to the incomplete removal of grain in the shaving operation.

Water absorption : For good chamois leather, it appears that Q24 hr. should be 300. The removal of grain by shaving should be thorough to ensure good water absorption properties and also sinking property. If the grain is not completely removed, the grain side will retard the uptake of water and it will take a long time to wet the grain. These considerations will also influence the sinking time for the different leathers.

Chemical Properties :

Acid soluble hide substance : From the results, the acid soluble hide substance seems to be of no great significance. But it would be better if these figures were as low as possible, say 1% as suggested by Booth and Mayer.[1]

Free fat : Free grease must be removed as thoroughly as possible to achieve easy wettability, quick sinking and high water absorption. If the grease content is high, water absorption will be less. Also, if the grease is considerable, the difference between the absorption after $\frac{1}{2}$ hour and 24 hours will be high. This cannot be said as a general rule, as the fibre structure and splitting up of fibres also have an influence on the water absorption.

Bound fat : In some cases, the bound grease seems to have a bearing on the water absorption, but it cannot be generalised. If the bound grease is more, the leather absorbs less water.

Table I.

(ANALYSIS OF CHAMOIS LEATHERS)

On 15% Moisture basis.

Percentages.

No.	Hide subs.	Acid sol. H.S	Free grease	Bound grease	HCHO	Total ash	Soluble ash	Insol. ash	Water sols.	pH of water sols.	W. A. Q ½ hr.	W. A. Q 24 hrs.	Sink test	Filter test
1.	75	1.39	1.515	2.94	0.116	2.98	0.552	2.43	1.575	6.4	295	313	2 hrs.	
2.	75.8	2.44	1.400	1.824	0.055	2.36	0.829	1.53	1.930	6.1	310	328	15 sec.	
3.	70.0	0.872	3.540	1.67	0.197	5.54	1.01	4.53	2.53	6.9				
4.	71.6	0.875	3.630	1.62	0.198	6.41	1.15	5.26	2.99	6.8	348	379	28 „	
5.	72.4	1.040	3.650	1.66	0.211	7.37	1.16	6.21	2.60	6.9				
6.	70.4	1.100	11.20	2.22	0.64	2.37	0.43	1.94	1.26	6.1				
7.	69.8	1.220	9.60	2.25	0.646	2.57	0.443	2.13	1.34	6.1	335	339	12 „	
8.	69.1	1.40	10.35	2.29	0.675	2.28	0.563	1.72	1.49	6.1				
9.	66.76	.232	9.499	5.363	0.1794	2.397	0.6797	1.717	1.601	9.3	296	309	15 „	
10.	68.17	.1467	10.370	3.916	0.476	2.443	1.429	1.014	2.880	9.25	298	300	12.5 „	
11.	69.31	.2599	6.322	2.939	0.4132	4.763	2.525	2.238	4.526	8.4	274	288	10 „	
12.	72.69	—	1.736	2.025	—	5.113	0.3289	4.784	4.564	9.6	331	345	12 „	
13.	71.09	—	2.845	2.596	—	8.081	1.249	6.832	2.613	8.2	—	—	—	
14.	67.32	—	0.2443	1.809	0.1022	12.95	0.3990	12.551	1.764	7.25	294	293	30 „	
15.	61.30	—	4.245	2.685	0.1209	14.83	0.4775	14.353	1.515	8.1	334	362	60 „	
16.	71.47	—	2.823	2.654	.08325	2.462	0.4258	2.036	1.597	7.0	276	293	20 „	Stands 6 min.
17.	59.61	—	8.486		0.1027	2.863	0.9475	1.916	2.894	7.15	216	250	2½ min.	Stands 3′ 10″
18.	74.37	—	2.870	1.277	0.5039	3.049	0.5125	2.536	1.837	8.4	242	247	3 „	Stands 8½
19.	69.88	—	2.183	1.734	0.2602	5.607	1.312	4.295	3.687	9.8	259	277	10 sec.	Does no stand 1′

Total ash : The total ash should not exceed 4%. Chalk is generally used in the buffing operation. Excessive loading is resorted to, to get the required wt./sq. ft. This practice should be discontinued.

Water solubles : Water solubles should be as low as possible. This indicates the thoroughness of washing after degreasing.

pH of water solubles : The pH of water solubles should be around 7.0, showing that all the excess alkali used in the degreasing and washing process has been completely removed. If it is more, it shows that the washing has not been thorough.

Conclusions :

Excluding some of the unusual values in the cases of high oil, ash contents etc., the ranges for chemical and physical characteristics of Indian chamois leathers may be taken as follows :

Ranges

	%
Moisture	15-20
Hide substance	65-75
Water sols	less than 4
Free fat	5-10
Bound fat	1-5
Insol. ash	2-6
Total ash	2-5
HCHO	nil—1
pH of water sols	6-8
Water absorption :	
$Q\frac{1}{2}$ hr.	200-325
Q24 hr.	250-400
Sink test	10 sec. —2 min.
Filter test (B.O.C.)	1 min.—5 min.

Acknowledgement.

This work was carried out at the instance of the Indian Standards Institution with whose kind co-operation, a number of chamois leather samples were collected. Our thanks are due to the Indian Standards Institution and to a number of tanners who sent samples of chamois leathers.

Chemistry & Physics Divn.,
Dated 3—4—1956.

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NEW BARKS FOR E.I. TANNAGE—II. PITHECOLOBIUM DULCE

M. K. UDAYA VARMA, E. C. MATHEW & B. M. DAS.

SUMMARY

Pithecolobium dulce bark when used alone produces a light coloured, full and strong leather. Blending with myrobalam in the proportion 6.5 : 1 (on weight basis) improves the colour. The best results are obtained by blending Pithecolobium dulce and konnam bark (5 : 8) on weight basis. This blended tannage produces a better leather than the traditional tannage using wattle and konnam. Pithecolobium dulce can be considered as a good substitute for wattle bark.

Pithecolobium dulce (*Kodukkapuli* Tamil, *Simachinta* Telugu) is very common especially as forming hedges which somewhat resembles hawthorn hedges. It is usually a small tree and often very slender, crooked and ill grown. It can be recognised by the horizontal weals round the gray smooth trunk. The leaves may be solitary but are generally in clusters and at the base of each leaf or cluster is a pair of spreading horns. The common petiole is slender and generally not more than an inch in length. From it branch two short slender stalks each of which bears two dull, green, unequal-sided leaflets. These leaflets are oblong or slightly oval and they run to about $2\frac{1}{2}$" in length. The common petiole and its branches end in little points. The flowers grow in small, woolly heads attached by short stalks to a common peduncle which may be several inches long. The inflorescence may be described as a racema of flower heads. The calyx and corolla are green but the flowers appear to be white or yellowish from the colour of the numerous, soft stamens which are about 1/3" long and are slightly tipped with green. The style is long, thread like and pink in colour. The pod is narrow, somewhat constricted between the seeds and twisted into rings. The end often looks like the sting of a scorpion to which resemblence the Tamil name is apparently due.[1]

The tannin content of the bark varies widely according to the age of the tree, analysis of a typical sample of the bark gave the following results.

Table I.

Moisture	9.3%
Tannin	25.2%
Non-tans	13.2%
Insolubles	52.3%
pH of analytical solution	4.8

Colour of analytical solution	Yellow 12 Red. 3.1
Ash content	5.16%
Sugars (Expressed as Glucose)	4.54
Free acid (to pH 5.8)	7.5 mgm. eqvt./100 gms. total solubles.
Total salts (resin method)	64.7 mgm. eqvts./100 gms. total solubles.

The tannin is of the catechol type.

A 20° BK liquor was prepared. Titration was carried out to pH 2.0 using N/2 HCl and pH 8.0 using N/2 NaOH and a titration curve drawn (Fig. 1).

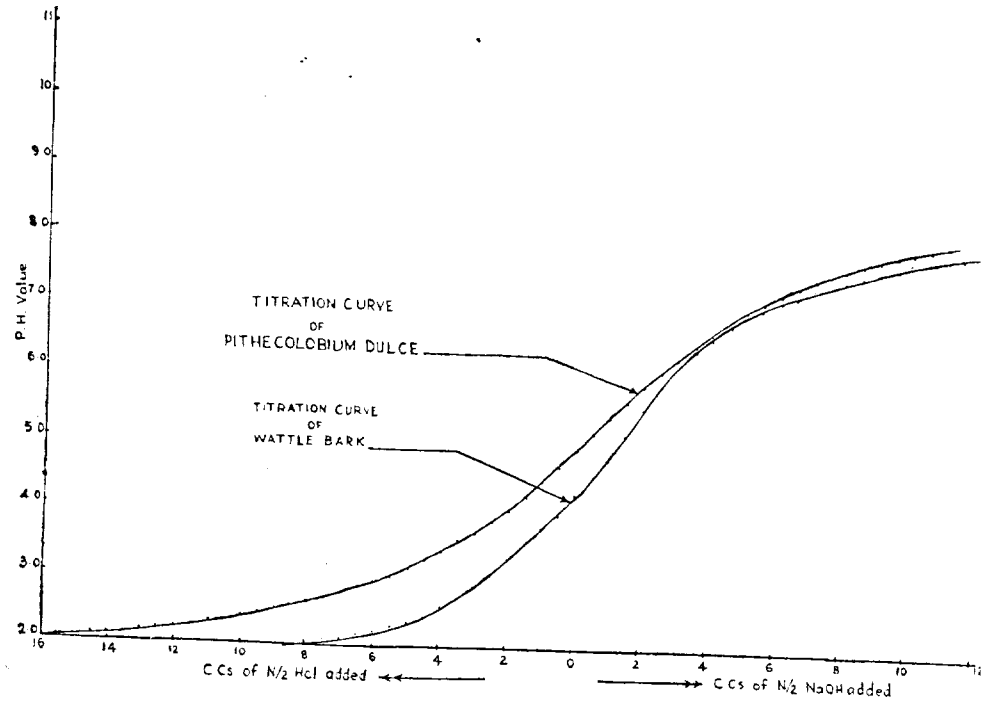

Fig. 1.

The titration curve of Pithecolobium dulce is similar to that of wattle but less steep. The curve in the range of its initial pH to pH 2.8 is flatter than that of wattle showing that the amount of salts of weak acids is more than that in wattle. The amount of weak acids (titrated to pH 5.8) is nearly the same as for wattle. A study of the titration curve shows that Pithecolobium dulce is better buffered and consequently a more mellow tanning material than wattle.

Leaching : 1 lb. of the bark was leached with four times its weight of water for 24 hours at room temperature. The liquor was drawn and an equal volume of fresh water was added. Thus leaching was done five times and the liquors from each leaching analysed. The results are given in Table II.

TABLE II.

	Total extracted in gms.	1st Leaching		2nd Leaching		3rd Leaching		4th Leaching		5th Leaching	
		Amount extracted in gms.	% of total	Amount extracted in gms.	% of total	Amount extracted in gms.	% of total	Amount extracted in gms.	% of total	Amount extracted in gms.	% of total
Solubles	79·68	35·62	44·7	17·65	22·15	11·06	13·88	9·05	11·36	6·3	7·91
Tannis	51·91	19·12	36·82	12·13	23·37	8·52	16·42	7·13	13·74	5·01	9·65
Non-tans	27·77	16·5	59·41	5·52	19·87	2·54	9·15	1·92	6·92	1·29	4·65

It is seen from this table that about 37% of the tannin is leached out on the first day itself and about 77% by the end of the third day.

PRACTICAL TANNING TRIALS.

Experiments were conducted to assess the suitability of this bark for the production of E.I. kips.

Pieces were cut from the butt portion of a wet salted cow hide which had been limed and delimed as for the usual E.I. tannage and the following tanning experiments done :

(i) Using Pithecolobium dulce bark alone.

(ii) Using a blend of Pithecolobium dulce bark and myrobalam in the proportion 4:1 on tannin basis.

(iii) Using a blend of Pithecolobium dulce bark and myrobalam in the proportion 3:1 on tannin basis.

(iv) Using a blend of Pithecolobium dulce bark and myrobalam in the proportion 2:1 on tannin basis.

Materials corresponding to 16% tannin on the pelt weight were soaked for the first bark. The tanning was started with a liquor of 6°BK. The bark was put in between pelt pieces. The pieces were handled daily and a second bark was given on the 8th day. For this materials corresponding to 8% tannin on the pelt weight were taken. The strength of the second bark liquor was adjusted to 7° BK. On the 15th day the pieces were taken, bleached with

a solution containing Perfectan O and oxalic acid and put in myrobalam liquor (15° BK). They were oiled on the 17th day and allowed to dry. A parallel experiment was also carried out with wattle bark and leathers obtained were compared. The results are given in Table III.

TABLE III.

Experiment	General appearance	Colour	Feel	Fullness	Crackiness	Remarks	Yield
I	Good	Light	Very soft	Full	No crack at double fold	Good	45%
II	Very good	Lighter than I and like the regular E I. tanned kips	Soft.	Full	do	Very good	41·1%
III	Good	Light	Soft	Full	do	Good	37·4%
IV	Good	Much improved colour	Soft	Full	do	Good	40·8%
Control	Good	Light but still reddish	Soft	Full	do	Good	40·3%

Tannage with this bark produces a fairly light coloured leather with full substance and soft feel. When a blend with myrob is used for tanning, the colour is much improved and this improvement is directly proportional to the amount of myrob used in the blend.

As it was found from the above experiments that Pithecolobium dulce bark alone and blended with myrob in the proportion 4:1 on tannin basis gave the best results these experiments were repeated with bigger lots.

Wet salted cow hides were limed and delimed as for the usual E.I. tannage. They were cut into sides and the left halves taken for control. As there was no old liquor, tanning materials equivalent to 16% tannin on the fleshed weight were used for the first bark and 8% for the second bark. For tanning the left halves (control) the blend was made up of 50% konnam bark, 25% Nilgiri wattle bark and 25% wattle extract (all on tannin basis), this being the blend generally used for E.I. tannage of kips. The materials were soaked in water on the day previous to the commencement of tanning. The liquors were adjusted to 7° BK and the tanning started. Beaming was done on the third and eighth days and the sides were put in to second bark liquor prepared by soaking the required quantity of materials in half of the old liquor on the previous day. The liquors were adjusted to 8°BK. They

were again beamed on the 10th day. On the 15th day the hides were washed and bleached with a solution containing Perfectan O and oxalic acid (2:1), beamed and put in myrobalam liquor of 25°BK. Another myrobing at 25°BK was done on the 17th day. Next day they were washed, beamed and oiled with gingelli oil. A solution containing 1% Epsom salt, 1% glucose and 2% corn flour on the expected yield was applied on the flesh side, set twice and dried. A comparison of the experimental leathers with the control is given in Table IV.

TABLE IV.

	General aprearance	Colour	Feel	Tightness of grain	Fullness	Tearing strength	Penetration	Crackiness
Pithecolobium dulce alone	Good	Slightly darker than control	Soft	Tight	Fuller	Good	Thorough & uniform	No crack at single fold
Pithecolobium dulce plus myrob (6·5:1) on wt. basis	Good	Slightly darker than control but lighter than above	Firm	Tighter	Full	Good	do	do
Control	Good	Cream colour	Firm	Tight	Full	Good	do	do

The yields were 47.6 for Pithecolobium dulce alone, 46% for Pithecolobium dulce and myrob and 44% for the control.

The leathers were analysed and the results are given in Table V.

TABLE V.

	Tannage with Pithecolobium dulce alone	Control	Tannage with Pithecolobium & myrob (6.5:1)	Control
Moisture	12.87	13.28	12.83	13.34
Oils & fats	5.84	5.67	6.02	5.43
Total ash	0.84	0.71	0.93	0.71
Water solubles	9.4	9.8	11.75	10.4
Ash of solubles	0.7	1.2	0.76	0.84
Insoluble ash	0.14	—	0.17	—
Hide substance	41.65	43.59	40.31	43.25
Fixed tans	30.1	27.66	28.92	27.58
Degree of tannage	72.3	63.5	71.7	63.77
pH of water solubles	3.65	3.55	3.6	3.6

Experiment was also carried out replacing wattle bark and wattle extract from the blend used for traditional E.I. tanning of kips with Pithecolobium dulce bark. A blend of Pithecolobium dulce bark and konnam bark (1:1) on tannin basis, was used. Tanning, myrobing etc. were done as for the previous experiment. Comparison of the leather with control showed that

(1) General appearance was better than that of control.

(2) Colour was good and lighter than that of control.

(3) Tightness of grain and fullness were equal to control.

(4) Yield is nearly the same as that of control (48.5 and 50).

Analytical data are given in Table VI.

TABLE VI.

	Tannage with Pithecolobium dulce and konnam	Control
Moisture	14.35	14.45
Oils & fats	5.75	4.77
Total ash	0.62	0.72
Water solubles	8.11	7.6
Ash of solubles	0.74	1.1
Insoluble ash	—	—
Hide substance	46.09	45.98
Fixed tans	25.7	27.2
Degree of tannage	55.76	59.16
pH of water solubles	4.1	4.2

Chemistry and Phys. Divn.

Dated 24—3—1956.

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INVESTIGATIONS ON MAKING GOOD LEATHER FROM DEAD HIDES FOR POLICE AND MILITARY BOOT UPPER

A. K. SEN GUPTA & B. M. DAS.

SUMMARY

This investigation was taken up in view of the campaign against cow slaughter with a view to work out a process for making such leather even from dead hides as can be used for making military and police boots. The processes described to this article are the results of this investigation.

Dead hides constitute a little above 7/8th of the total production of cow hides in India (i.e. 12,227,000 pieces in 14,156,000 pieces). Their proper utilisation has so far been a perplexing problem to the tanners. It is a popular saying amongst those engaged in leather industry that dead hides are unsuitable for shoe upper leather because of the many serious inherent defects which cause sponginess of structure and looseness of grain. What are the structural changes associated with the death of the animal is a subject of histological research, but in addition to these we have sufficient reasons to impute some bacterial damages to them due to their delayed flaying and curing. We know that hides and skins are protein bodies and are subjected to bacterial damages along with the death of the animals. The object of curing hides immediately after the death and flaying of the carcases is to avoid this bacterial damage. In all cases of slaughtering, the slaughtered body is immediately flayed in the interest of meat and the hide reaches the dealer's godown where it is immediately taken care of and cured. But the picture is entirely different in case of a dead animal. The carcase of a naturally dead animal is regarded as obnoxious and disgusting and none but a person of the chamar or muchi community would touch it. Consequently the carcases are allowed to lie in the fields where the animals have fallen dead until a muchi or a chamar arrives there to flay them. A good deal of time elapses between death and flaying and curing which in most cases is sufficiently long to set up bacterial action, with consequent loss of hide substance which is mainly responsible for the sponginess and looseness of the grain of the leathers produced from dead hides. Very often the bacteria develops along

the blood vessel systems causing the destruction of hide fibres in the vicinities of blood vessels. Destruction follows the pattern of blood vessels and the leather produced from such stock is called by the tanner to be veiny. When it extends to sweat glands, the leather produced is loose and pipey. Apart from the changes of this bacterial damage, the carcase is often taken to the 'Vagar' by dragging along streets and lanes and sometimes through thorny jungles which causes irreparable damage to the grain by scratches and abrasion. Moreover if the carcase be laid in the 'Vagar' for sometime, vultures and other birds prey upon it and the hides are damaged by the scratches of their nails. For all these defects dead hides are not liked by tanners. But we should remember that they being the major part of the production of cattle hides in India, their proper utilisation is of vital importance to the Indian tanning industry in particular and Indian economy in general. The importance of solving the problem of tanning hides of dead cattle by research has been emphasised by Fialka. So, the Central Leather Research Institute undertook research for developing techniques of tanning the dead hides which may produce uppers of satisfactory marketable leather from dead hides specially ammunition and police boots. As a result of this research the following processes have been developed.

PROCESS I :

Soaking : The hides should be carefully examined before they are put to the soaking process. It is better not to soak them if their condition does not justify soaking. It can be taken as a general rule that green and wet salted fallen stocks need not be soaked at all.

Trimming, washing and weighing : The hides are trimmed to proper shape, washed in paddle with 3 changes of water, unloaded, weighed and then put to the depilating process.

Depilation : This is done in a paddle by two-bath process for seven hours with the following :

Sodium sulphide—6% on the soaked wt. of the hides.

Water—380% on the soaked wt. of the hides.

The sodium sulphide is dissolved in hot water and the solution is cooled. The cold solution is added gradually to the bath during a period of 2 hours and the paddle is continued to run for 3 hours more after the addition of the entire quantity of sulphide solution. The pH of the bath after complete addition of sulphide is 8.5.

The hair is dissolved by the sulphide solution. The unhaired stock is unloaded, washed thoroughly, hides cut into sides, fleshed, scudded well and put to the second bath made with

Calcium chloride	—	5% on the soaked wt. of the hides.
Water	—	380% „ „

The pre-dissolved calcium chloride is added slowly into the bath during a period of ½ an hour and the paddle is continued to run for 1½ hours or more after the addition. The stock is unloaded and examined.

Observation : The pelt is very tight and full with a clean surface and the swelling is satisfactorily repressed.

Deliming and Bating : Deliming and bating are done in one operation in the same bath with the following :

Ammonium sulphate	—	½% on unhaired pelt weight.
Pancreol 3A	—	1% „ „
Water	—	380% „ „

Water is taken into the paddle and the fallen pelt from the chloride bath is put into it and the paddle is set running. The pre-dissolved bate and ammonium sulphate in water are added to the paddle during a period of 15 minutes and the paddle is continued to run for ½ an hour longer after the addition. Sulphuric acid is now added to the bath very cautiously to make the pH 7.7 and the paddle is run for ½ an hour. The stock is unloaded, scudded well and immediately put to pickling.

Observation : Reducing the pH to 7.7 at the end with the addition of sulphuric acid has two-fold objects, viz., (1) the pelt attains its maximum falling ; (ii) the enzyme bate becomes most active. Hence the bating is completed with the maintenance of all the desirable properties of the pelt.

Pickling : Pickling is done in a drum with the following :

Sulphuric acid (Sp-Gr. 1.84)	—	2% on unhaired pelt wt.
Aluminium sulphate	—	1¼% „ „
Common salt	—	25% „ „
Water	—	40% „ „

The well scudded pelt is taken in a drum, common salt is added to it and the drum is set in motion. Pre-dissolved and cooled

sulphuric acid and aluminium sulphate in the requisite quantity of water (i.e. 40%), is added slowly into the drum during a period of one hour. The drum is continued to run for 2 hours more after the addition and kept overnight with mouth open. Next morning the drum is run for ½ an hour and the stock is unloaded and horsed up immediately for complete draining of the liquor. Next morning the stock is put to the chrome tanning process.

Observations : It is observed that if the pickling is done for a longer period with proper amount of acid and salt, acid-fixation is better with the result that the subsequent chromium uptake is more, quicker and uniform all over the pelt. The resulting leather is soft and smooth with a round feel.

Chrome tanning : The well-pickled stock is chrome tanned in a drum with a liquor of the following composition :

Sodium bichromate	100 parts
Sulphuric acid (S.G. 1.84)	100 parts
Molasses	100 parts
Water	400 parts

The liquor is 29% basic and is made a week before use. Chrome liquor equivalent to 2½% bichromate on the pickled pelt is used. Just a day before the use of this liquor 1% Gum Tragon (on the pickled wt.) is made into solution with boiling water and kept mixed with the requisite quantity of the chrome liquor to be used (i.e. 2½%). The Tragon-mixed chrome liquor is then put into the pickled stock taken in an empty drum in a slow stream through the hollow axle during a period of one hour. The dilution of the entire liquor in the drum is made to 40% on the pelt. The object of using gum Tragon is to fill up the emptyness in the hide structure caused by bacterial action on the dead hides leading to a loss of hide substance. By this filling the looseness of grain and lack of substance in leather made from dead hides are counteracted and the quality of the finished leather considerably improved. The drum is run for 2 hours more after the addition entire quantity of chrome liquor and the complete penetration of chrome is tested in a thick cut piece. The pH of the liquor is now immediately adjusted to 3.2 with 3% soda ash (on the pickled wt.) and the drum is run for an hour more and kept overnight with mouth open.

Next morning the drum is run for 15 minutes only, boiling test is performed and the stock is immediately unloaded and horsed up grain to grain and kept overnight.

Sammying, splitting and shaving : On the following morning the tanned stock is sammed, split between 3.5 and 4 mm. depending upon the thickness of the stock and shaved to maximum thickness with as uniform a substance as possible.

Retanning with chrome : The shaved leathers are taken in a drum and retanned with the following :

Chrome liquor	(made according to the proportions described above) equivalent to 1½% bichromate on the shaved weight.
Water	38½% on the shaved weight.

The well diluted liquor (made with the requisite quantity of water) is added to the shaved stock taken in a drum in a slow stream through the hollow axle and the drum is continued to run for 2 hours more after the addition. The leather is then immediately neutralised with :

Hypo	— 2%	on the shaved wt. of the leather.
Sodium bichromate	— 2%	do.
Water	— 30%	do.

The well diluted neutralising mixture (made with the requisite quantity of water) is added into the drum in a slow stream through the hollow axle over a period of one hour and the drum is continued to run for an hour more after the addition and kept overnight with mouth open. Next morning the drum is run for 15 minutes only, chrome liquor run out and the leather washed with water at room temperature and sorted for Blacks and Browns.

Observation : The leathers are very full with fine grain, tight and heavy.

Dyeing and fatliquoring : (i) For Browns : Dyeing is done in a drum at 40°C for ½ an hour with the following :

Naphthalene leather brown ADS	—	14 oz%	on the shaved wt.
„ Orange G. 132		2 oz%	do.
„ Water at 60°C		75%	do.

When the dye-bath is clear, it is drained. The stock is now mordanted for one hour with :

Cube gambier	— 1½% on the shaved wt.
Water at room temperature	— 75% on the shaved wt.

When the mordant bath is clear, it is drained. The stock is now fatliquored for one hour with :

Castor oil	1.58%	on the shaved wt.	
Fish oil	1.25%	„	
Cremol F	1.25%	„	
Sulpholine oil P.	3%	„	
Casein	1%	„	(Preparation of casein solution :
Water	75%	„	

Casein	80 pts.
Borax	4 pts.
Ammonia	10 pts.
Water to	800 pts.)

Casein is soaked overnight in the requisite quantity of water in the following morning the temperature is raised to 50°C and the borax and ammonia added and stirred well.

When the fatliquor bath is clear, the stock is immediately horsed up grain to grain and kept overnight. If necessary the pH of the bath may be brought down to 6.4 by the addition of ¼% sulphuric acid (Sp. Gr. 1.84) on the shaved wt. and running the drum for 5 minutes only before the stock is horsed up.

Observation : Leathers are tight with smooth grain. A certain amount of free fat remains on the top which is absorbed during the course of sammying rendering the grain smooth and non-greasy. So a free layer of fat on the grain is very useful for the improvement of feel and characteristic grain pattern of the finished leathers.

(ii) *For Blacks* : Dyeing is done in a drum at 50°C for ½ an hour with the following :

naphthalene Leather carbon GS	1%	on the shaved wt.
Water at 70°C	75%	Do.

When the dye bath is clear, it is drained. The stock is now fatliquored for one hour as in (i).

Sammying and setting : Next morning the dyed and fatliquored leathers are sammed and well set out by the machine.

Drying, sawdusting, staking, nailing, trimming and buffing :

The well set out stock is allowed to dry out completely. The dry leathers are sawdusted overnight, staked, toggled on frames or nailed on boards, dried trimmed round the edges and buffed. The stock is now put to the finishing operation. Before finishing the

buffed leathers are sorted into 2 categories viz. (i) leathers with sound and (ii) leathers with damaged grain. Leathers with sound grain are finished as usual but the leathers with damaged grain are again subdivided into two categories viz., those with slight and those with deep damages. Light damages are evened out by snuffing the grain but retaining the grain pattern in tact and finishing with the application of a special finish made from synthetic resin etc. But in the case of deep damages the recourse is taken to print the leather with shark grain or zug grain to conceal the grain damage.

These finishing processes are described below :

FINISHING—(a) BROWNS.

(i) *For sound grained leathers.*

1st Season :

Carpenol pigment	No. 5004	1 lb.	
Do.	No. 7	3 lbs.	
Naphthalene Leather Brown ADS		72 gms.	
„ Bordeux		40 gms.	
7½% casein solution		5 lbs.	(Composition of casein
Carnauba wax emulsion		8 oz.	solution :
Glycerine		4 oz.	Casein 7½ pts.
Formaldehyde		1½ lbs.	Borax 3/8 pts.
Water to 4 gallons.			Ammonia 15/16 pts.
			Water to 100 pts.)

Process : Casein is soaked overnight in the requisite quantity of water in the following morning the temperature is raised to 50°C and the borax and ammonia added and stirred well.

One coat of the finish is applied with a velvet pad and the leathers are allowed to dry out in the shed.

2nd Season :

Carpenol pigment	No. 5004	1 lb.	
Do.	No. 7	3 lbs.	
Naphthalene Leather Brown ADS		72 gms.	
„ Bordeux		40 gms.	
7½% casein solution		5 lbs.	(Composition of casein solution and process as in 1st season.)
10% Gum Tragacanth solution		8 oz.	
Glycerine		4 oz.	
Formaldehyde		1½ lbs.	
Water to 4 gallons.			

One coat of the finish is applied by spray and the leathers are allowed to dry out in the shed.

Spray season :

Carpenol pigment No. 5004	1 lb.	
Do. No. 7	3 lbs.	
Naphthalene Leather Brown ADS	72 gms.	
„ Bordeux	40 gms.	
7½% casein solution	5 lbs.	(Composition of casein solution and process as in 1st season.)
Glycerine	4 oz.	
Formaldehyde	1½ lbs.	
Water to 4 gallons.		

One coat of the finish is applied with a velvet pad and the leathers are allowed to dry out in the shed.

Fixing coat :

7½% casein solution	¾ gallon	(Composition of casein solution and process as in 1st season.)
Formaldehyde	¾ gallon	

Mixed together and then one coat is applied by spray, and the leathers are piled overnight. Next morning the leathers are dried, glazed, measured and hot plated.

(ii) *For corrected—Grain and *Deep damaged-grain leathers.*

Season :

*Earnshaw Dark Brown Pigment Paste	2 lbs.	
*Earnshaw Light Brown Pigment Paste	1 lb.	
Neran Brilliant Brown	20 gms.	
Coomassie Red PGS	8 gms.	
7½% casein solution	1¼ lb.	(Composition of casein
Aqueous resin emulsion	2½ lbs.	solution and process
Diethylene Glycol	4 oz.	as in 1st season.)

(*3 oz. Powder is made up to 1 lb. paste with hot water. In case of badly damaged grain 2 sizing coats consisting of gum Tragon—1¼ oz., Naphthalene Leather Brown ADS—4 oz., Linseed oil—4 oz., water to 15 lbs. are applied first and then the seasoning follows).

Two coats of the finish are applied with a velvet pad and the leathers are allowed to dry out in the shed. Next two coats are applied by spray and the leathers are again allowed to dry out in the shed.

Clear coat :

7½% casein solution	12 oz.	(Composition of casein
Egg albumen	6 oz.	solution and process
Formaldehyde	8 oz.	as in 1st season.)
Water	2¼ lbs.	

Mixed together and then one coat is applied by spray and the leathers are piled overnight. Next morning the leathers are dried and assorted onto (i) corrected-grain and (ii) deep damaged-grain. Corrected grain leathers are simply measured and then hot plated, but deep damaged-grain leathers are printed with a shark grain plate at 200°F with a pressure of 250 Kg per sq. cm. Duration of pressure is ½ minute for each side. A side of 3 mm. thickness becomes 2.5 mm. after embossing.

(b) For Blacks.

(i) *For sound-grained leathers* :

Season :

Nigrosine G 140	1 oz.	
Bright Black Pigment paste	8 oz.	
7½% casein solution	1 lb.	(Composition of casein
Plasticiser (Boston)	2 oz.	solution and process
Liquor ammonia	2 oz.	as in 1st season.)
Formaldehyde	6 oz.	
Water to 1 gallon.		

Two coats of the finish are applied with a velvet pad and the leathers are dried, glazed, measured and hot plated.

(ii) *For corrected—Grain and *Deep damaged-grain leathers.*

Season :

Bright Black Pigment paste	8 oz.	
Nigrosine G 140	1 oz.	
7½% casein solution	1 lb.	(Composition of casein
Aqueous resin emulsion	8 oz.	solution and process
Diethylene Glycol	2 oz.	as in 1st season.)
Water to 1 gallon.		

*(In case of badly damaged grain 2 sizing coats consisting of Gum Tragon—1¼ oz., Nigrosine—4 oz., Linseed oil—4 oz., Water to 15 lbs. are first applied and then the seasoning follows).

Two coats of the finish are applied with a velvet pad, and the leathers are allowed to dry out in the shed. Next two coats are applied by spray and the leathers are again allowed to dry out in the shed.

Clear coat :

7½% Casein solution	12 oz.	(Composition of casein
Egg Albumen	6 oz.	solution and process
Formaldehyde	8 oz.	as in 1st season.)
Water	2½ lbs.	

Mixed together and then one coat is applied by spray and the leathers are piled overnight. Next morning the leathers are dried and assorted into (i) corrected grain and (ii) deep damaged-grain. Corrected-grain leathers simply measured and then hot plated but deep damaged-grain leathers are printed with zug grain plate at 200°F with pressure of 250 kg per sq. cm. Duration of pressure is ½ minute for each side. A side of 3 mm. thickness becomes 2:5 mm. after embossing.

PROCESS II :

Almost same as Process I except the following changes.

Chrome Tanning : After the penetration of chrome is complete as tested by cutting the thickest portion of a side, 5% Trionol EB on the pickled wt. emulsified with 5 times its volume of water is added to the drum and the drum is run for an hour more and then the pH is immediately raised to 3.2 with the addition of 3% soda ash. Rest of the process is same as Process I.

Fatliquoring : Fatliquoring of the stock is done only with ½% leather Olinor DR 9 on the shaved weight for ½ an hour only maintaining its concentration, temperature etc., as Process I. Rest of this process as well as all other subsequent proceses are same as Process I.

Observation on the finished stock : Except fulness which is considerably lower, all other properties can be very well compared with those produced by Process I.

Tanning
and
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STUDIES ON THE TANNING CHARACTERISTICS OF MODIFIED WASTE SULPHITE LIQUORS

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SUMMARY

Sodium Lignosulphonate obtained from waste sulfite liquors has been condensed with resorcinol to yield a soluble product which is found to possess much improved tanning properties. The tanning property of this modified lignosulphonate, however, is influenced considerably by a number of factors such as the conditions of condensation, pH and concentration of the tanning bath etc. All these have been thoroughly investigated *vis-a-vis* the tanning characteristics of the final product.

The importance of Lignin as a raw material for potential tanning agents has been widely recognised since the publication of an article by Lipsitz, Lollar, and O'Flaherty,[1] who were led by the Hydrogen bonding theory of tannage to evolve a more successful application of Lignin derivatives to the tanning industry.

The absence of any real tanning properties in Lignin has been discussed by a number of investigators [2, 3] who were in general agreement that this was due to the relatively low ratio of phenolic-OH groups.

Freudenberg,[4] while comparing the structure of Lignin with that of the Natural tannins arrived at the conclusion that Tanning by Lignin Sulphonic acid was attributed to the presence of sulphonic and phenolic hydroxyl groups, although it contains a smaller percentage of the latter than the natural tannins. The presence of secondary and tertiary alcoholic-OH groups in the molecule of Lignin sulphonic acid stands in the way of effecting a successful tannage with it alone, although it is conducive to the increased solubility and diffusibility of the product. These alcoholic-OH groups tend to impart undesirable hydrophilic characteristics to leather tanned with Lignin sulphonic acid only. According to 'Gustavson '[5] the decreased hydrothermal stability of the hide after treating with Lignin sulphonic acid is due to the structural peculiarities of the Lignin molecule, such as the inadequate number of phenolic hydroxyl groups, rather than the molecular size.

Tu and Lollar[6] have recently shown that only those hydroxy derivatives of Benzhydrol, Benzophenone, di-and triphenyl methane and Xanthene which can take part in quinoid resonance are possessed of good tanning properties. They also conclude that this quinoid resonance enhances hydrogen bonding, thus offering evidence for the hydrogen bonding mechanism in phenolic tannages.

This work of Tu and Lollar evidently suggests that proper chemical modification of Lignin derivatives would result in an improved product, which would overcome the objections associated with the use of unmodified Lignin.

Amongst the methods, used by ' Lipsitz and Lollar '[7] to increase the phenolic hydroxyl content of magnesium Ligninsulphonates and of both soft wood and hard wood alkali Lignins, condensation with Resorcinol and phenol resulted in derivatives with greatly improved tanning properties. However, the products prepared in this way were insoluble in water and hence were either sulfited to make them more water soluble or their tanning capacity was assessed by means of a solvent tannage. Since the solvent tannage systems, however, are impractical under present conditions in the tannery, and the additional processing cost involved in imparting water solubility to the modified Lignins rules out the process as uneconomical.

Very recently ' Marshall and Krizsan '[3] have shown by their careful investigation, that Lignin sulphonic acid can be condensed with phenols and cresols under conditions much less rigorous than were thought to be necessary. They also discovered that anhydrous conditions were not necessary to effect a condensation between decationised Lignin sulphonates and phenol. It is, however, clear by a critical study of their work that the Lignin sulphonic acid—Resorcinol condensate does give a better yield and feel to leather as well as improves its hydrothermal stability. This is most probably due to the fact that in case of Resorcinol-condensation, a larger number of phenolic hydroxyl groups enter the composition of Lignin sulphonic acid as compared to the phenolation of waste sulphite liquor.

This improvement of Lignin sulphonate-Resorcinol condensate over phenolated Lignin sulphonic acid led us to investigate the probability of preparing a water-soluble product by choosing a suitable Lignin sulphonic acid salt and carefully controlling the various factors which govern the condensation. In their paper,

Marshall and Krizsan while mentioning the properties of Lignin sulphuric acid-Resorcinal condensate, do not comment on the solubility or otherwise of their product in water.

Since Lipsitz and Lollar, (loc. cit) used the Magnesium salt of Lignin sulphonic acid in their experiments and got insoluble products, it was presumed that a sodium Lignin sulphonate might give a soluble condensation product with Resorcinol because of the universal solubility of Sodium salts. The results of preliminary work in our Laboratory indicated that sodium-Lignin sulphonate could be condensed with resorcinol under certain conditions to yield a water soluble product while the Magnesium salt of Lignin sulphonic acid yielded an insoluble product under identical conditions. Moreover, it was observed that the reaction when carried out in aqueous medium yielded a product which was not found to possess much improved tanning properties.

Experimental

The raw material used in all our investigations was a commercial waste sulfite liquor, kindly supplied by Messrs. India Paper Pulp Co. Ltd., Calcutta. No attempt was made to remove the residual sugars etc., since the presence of small amounts of these substances during the tanning process has never been considered to be detrimental. The waste sulfite liquor used by us consisted principally of magnesium Lignin sulphonate, which was always converted to the sodium salt before the condensation was carried out.

Conversion to Sodium salt : The conversion of Magnesium salt to the sodium salt was effected by double decomposition with sodium carbonate at atmospheric temperature, thereby precipitating Magnesium as its carbonate from the solution. A concentrated solution of commercial sodium carbonate was gradually added to the concentrated waste sulfite liquor with stirring until the formation of Magnesium carbonate precipitate seemed to stop. The mixture was thoroughly stirred and kept overnight. Next morning the ppt. was separated from clear solution by centrifugation and concentrated Sodium Carbonate solution was further added to the clear solution until complete precipitation. The clear solution until complete precipitation. The clear solution obtained after centrifugation mainly contained the sodium salt of Lignin sulphonic acid along with some excess of Sodium Carbonate. The solution was brought to a pH of 7 by slowly adding Hydrochloric acid (dil) and then dried in a spray drier to a fine powder.

Condensation : The general procedure for the preparation of the Lignin-resorcinol condensate was as follows :—

Equal weights of the dry lignin material and Resorcinol were intimately mixed and placed in a flask fitted with a reflux condenser and a thermometer. A little ethyl ether was added to the mixture to bring it to a pasty mass, and then a volume of concentrated Hyderochloric acid equal to 10% of the Lignin weight was added. The mixture was heated to 130°C and allowed to reflux for 3-4 hrs., after which the resinous mass was poured in water to get a clear solution. Yield of about 100% based on the Lignin taken was usually obtained.

Effect of Temperature on condensation of Sodium salt of Lignin sulphonic acid with Resorcinol :—

The condensation of Resorcinol with Lignin sulphonic acid does not go to completion at the temperature mentioned above. At higher temperatures, though the extent of condensation is more, the solubility of the product decreases with the increasing degree of condensation. Our preferred conditions are designed to produce a completely soluble product with a maximum degree of condensation. It is important at this stage to mention that for these experiments the degree of condensation only signifies the number of gms. of resorcinol which have condensed with 100 gms. of waste sulfite liquor solids. This was determined by extracting out the free Resorcinol from a weighed amount of condensate by means of ether.

TABLE No. 1.

Degree of Condensation at various temperatures

Expt. No.	*Temperature of condensation*	*Degree of Condensation.*
A	100°C	16.04
B	110°C	21.50
C	120°C	31.54
D	130°C	25.94
E	135°C	26.50
F	140°C	30.38

The reaction was carried out in each case under identical conditions except for the temperature. As may be concluded from above, the degree of condensation was found to be maximum at 120°C and 140°C.

Rate and Degree of Fixation by hide powder, of various condensates obtained at different temperatures :—

For these experiments 2 gms. of hide powder previously soaked in water was treated in a bottle with 200 c.c. of a 20°Bk solution of each condensate at pH 3. All the bottles were kept in shaker. After 2 hours of shaking, half the quantity of hide powder was withdrawn in all the cases and the rest was shaken for further 22 hrs. in the same manner. All the samples of hide powder were dried under identical conditions for a day. The dried samples were then weighed and transferred to measuring cylinders to which a calculated quantity of water, based on the tanned hide powder weights was added. For every 1 gm. of tanned hide powder 100 gms. of water were taken. The washables were thus allowed to diffuse through the water-column in the measuring cylinders for 24 hrs. after which all the samples were filtered through Buchner funnel and the wash liquor sucked off under identical conditions. The samples were then sandwitched between pieces of blotting paper and allowed dry at room temperature. After two days the hide powder samples were found to be completely dry. From these, weighed amounts of hide powder were taken for nitrogen estimation by 'Kjeldahl method', as well as for moisture determination. Moisture content of each sample was determined by heating a weighed amount of it in an air oven until constant weight.

The remaining hide powder in the shaker was taken out from Tan-liquor after 24 hrs., and treated in the same way as above for nitrogen and moisture determinations. The results of the experiments are given in Table II.

TABLE No. II.

Rate and Degree of Tannage for various condensates.

Expt. No.	*Temp. of condensation.*	*Degree of Tannage....* *After 2 hours of tanning.*	*After 24 hrs. of tanning.*
1.	100°C	34.4	43.82
2.	110°C	34.94	47.62
3.	120°C	31.37	43.90
4.	130°C	36.11	53.14
5.	135°C	33.40	45.41
6.	140°C	45.64	47.38

These observations show that the condensate obtained at 130°C is fixed to a maximum degree at a maximum rate too. The rate of tannage is minimum in case of 140°-Condensate (Expt. 6), while in the Expt. 3 (120°C) although the rate of tanning is satisfactory, the fixation is minimum.

Penetration of various condensates :

A 5% solution of pure gelatin was prepared and taken into graduated cylinders, which were kept in the Refrigerator for setting the ' gel '. 20 cc. of a 10°Bk. solution at pH 3 of the various condensates obtained at different temperatures were added to the gelatin gels in the cylinders and the initial readings noted. All the cylinders were maintained at a low temperature in the Refrigerater while the solutions were allowed to diffuse through the gel. At regular intervals, the level of the tan-solution in all the cylinders was read. The data obtained are given in the following table :—

TABLE III.

Rate of Penetration.

Expt. No.	Temp. of condensation	Initial Reading	Penetration after different periods of time							
			4 hrs.	16 hrs.	19 hrs.	23 hrs.	47 hrs.	51 hrs.	63 hrs.	69 hrs.
1	100°C	100cc	1cc	2cc	3cc	3cc	4cc	4cc	4·5cc	5cc
2	110°C	99cc	1cc	2cc	3cc	3cc	3·5cc	3·5cc	5cc	5·5cc
3	120°C	100cc	2cc	3cc	4cc	4cc	4·5cc	5cc	6cc	7cc
4	130°C	100cc	1cc	2·5cc	3·5cc	4cc	5cc	5cc	5·5cc	6cc
5	135°C	100cc	1·5cc	2·5cc	3cc	3cc	4·5cc	4·5cc	5cc	5cc
6	140°C	99·5cc	2cc	3·5cc	3·5cc	4·5cc	6·5cc	6·5cc	6·5cc	6·5cc

It is evident from the readings obtained as above that maximum penetration occurs in Expts. 3 and 6. Penetration of the condensate obtained at 130°C is less than that of those obtained at 120°C and 140°C.

Tanning by various products obtained at different temperatures:

Acetone dehydrated pieces of goat skin from the butt portion were put in 250 cc. of 10°Bk solution of different condensates at pH 3. The product obtained at 100°C penetrated completely after only two days, whereas those obtained at other temperatures showed incomplete penetration. The strength of the tanning solution in all the cases was then increased to 20°Bk and after two

days the skin pieces were again tested for penetration. The penetration was still found to be incomplete in all the cases, except in that of the product obtained at 130°C, which showed a comparatively quicker rate of penetration. On the fourth day the liquors were raised to 30°Bk strength. The penetration was found to be complete on the 6th day but the pieces were kept immersed in the Tan-liquor for one more day to ensure fixation. After this the leather pieces were taken out of the liquors, washed with water and slicked out. At this stage the shrinkage temperatures of all the leathers were determined. The leather pieces were then oiled by groundnut oil, and dried in a shady place. After drying they were staked and kept for further examination. A few of the physical properties observed are mentioned below.

TABLE IV.

Properties of leathers tanned by different condensates.

Expt. No.	*Temp. of Condensation.*	*Feel of leather.*	*Colour*	*Shrinkage temp.*
1.	100°C	Papery	Grey	63°C
2.	110°C	Hard	Brown	67°C
3.	120°C	Rough	Yellowish brown	66°C
4.	130°C	Excellent	Light brown	70°C
5.	135°C	Good	Brown	72°C
6.	140°C	Excellent	Dark Brown	70°C

1. The shrinkage temperature of Acetone dehydrated hide : 56°C
2. „ „ „ untreated sulphate Lye tanned leather : 58°C

The leather obtained in Expt. (4) was the best in all respects. It does not crack, while those obtained in Expt. (6) and (1) were very cracky. Hence subsequent experiments were carried out with the condensate obtained at 130°C.

Effect of pH on Fixation of Tannins in case of condensate, produced at 130°C :—For this series of experiments one gm. of hide powder was treated with 100 c.c. of a 20°Bk solution of the condensate at different pH values, ranging from 2.5 to 6, all other conditions remaining the same. Tanning was done for 24 hrs., after which the samples were treated in exactly the same manner as in previous experiments for nitrogen estimation. The results are listed below :—

TABLE V.

Expt. No.	*pH at which Tanning was done.*	*Tannin Fixed.*
1.	2.5	43.77%
2.	3	42.09%
3.	3.5	37.87%
4.	4	39.40%
5.	5	28.19%
6.	6	33.01%

At pH 5, fixation is minimum, but it is maximum at pH 2.5. Increase in fixation occurs above the isoelectric point also.

Optimum pH for Penetration of the condensate produced at 130°C :—A 5% solution of pure gelatin in water was prepared. The pH values of the solutions ranging from 2.5-6 were adjusted by adding the requisite quantity of a dilute solution of Tartaric acid in case of lower values of pH and by a dilute solution of sodium Hydroxide for higher values. The solutions of different pH were then transferred to graduated cylinders, which were kept in Frigidaire until the solution set into gels. 20 c.c. of a 10°Bk solution of the condensate having the same pH as that of the gel were added to each of the cylinders and their readings noted. The cylinders were again kept in the Frigidaire and the readings noted after regular intervals.

TABLE VI.

Expt. No.	pH of the tan-soln. and the gel.	Initial Read-ings	Penetration after different periods					
			15 hrs.	19 hrs.	23 hrs.	39 hrs.	43 hrs.	87 hrs.
1	6	99cc	4cc	5cc	5·5cc	6cc	6cc	8cc
2	5	99cc	3cc	4cc	4cc	5cc	5·5cc	6cc
3	4	99cc	2cc	2cc	2cc	3cc	3cc	4·5cc
4	3·5	99cc	2cc	2cc	2cc	2·5cc	2·5cc	5cc
5	3	100cc	2cc	2·5cc	3cc	3cc	3cc	4cc
6	2·5	100cc	3cc	3·5cc	4cc	4cc	4·5cc	5cc

It is evident from the above table that the optimum pH for the product used in the Experiment is '6'.

Effect of Concentration of the Condensate on Fixation :—For this purpose 1 gm. of hide powder was treated with 100 c.c. of the solution at pH 3, containing different amounts of the condensate (obtained at 130°C) and the amount of Tannin fixed in each case was determined in the same way as in previous experiments. The results obtained are given below :

TABLE VII.

Fixation/Concentration.

Expt. No.	*Concentration of solution.*	*Approximate* Bk.°	*Degree of Tannage.*
1.	1.8208%	5°Bk	30.89
2.	3.2672%	10°Bk	33.98
3.	4.2912%	15°Bk	42.59
4.	5.7880%	20°Bk	45.77
5.	7.4672%	25°Bk	47.97
6.	8.6136%	30°Bk	49.43

The results of this experiment indicate clearly that maximum degree of tannage is attained at a concentration of 4% or 8% in the case of this particular product.

DISCUSSION

Looking into the Table I, we find that the Degree of condensation i.e., the amount of Resorcinol condensed with 100 gms. of Lignin sulphonic acid, increases as the temperature of reaction increases from 100°C to 120°C. With a further rise of temperature the degree of condensation decreases (as found at 130°C) but is found to increase again with the temperature upto 140°. It is apparent, therefore that the condensation is maximum at an optimum temperature of 120°C, while at 140°C, the degree of condensation is only a little less than its value at 120°C.

Now, if we correlate the results of the Tables I and II, it becomes clear that the rate of tanning as well as the extent of fixation is optimum in case of condensate obtained at 130°C; but it is much less when the product obtained at 140°C is used. This can be accounted for by the fact that with the increasing amount of condensation the molecules become more and more unstable, as a result of which surface precipitation occurs as soon as they come in contact with the hide protein ; a phenomenon comparable

to that of ' case-hardening ' experienced with hides and skins. The bigger molecules thus, block the fine capillaries of the hide, restricting thereby the penetration of the tan-material any further, which subsequently gives low value of fixation. With the same reasoning, the product got at 120°C with highest degree of condensation should show still low rate of fixation, which on the other hand is found to be considerably high in the actual experiment. We may explain this on the ground that at 120°C, though the amount of resorcinol condensed with Ligninsulphonic acid is greater, the growth of individual molecules does not proceed as far as in the case of condensation at 140°C. It appears, therefore, that the normal rate of fixation of the material obtained at 120°C is only due to the smaller particle size and their greater stability. At higher temperatures, though the degree of condensation decreases, the growth of individual molecules proceeds to a greater extent, and this accounts for the decreasing stability of the materials in solution with the rise of reaction-temperature. The higher the reaction temperature the easier it is to precipitate the substance out of the solution by slight changes of pH and so on. At 140°C, however, we get a product of bigger particle size and with a high value for degree of condensation too. This explains the remarkable unstability of the molecules resulting in the low rate of fixation in the particular case. It has also been experienced that the condensate is rendered partly insoluble by carrying out the reaction at temperatures above 140°C.

The study of the comparative rates of diffusion of the various condensates through gelatin gel shows that the maximum value is obtained in the case of products prepared at 120°C and 140°C, while it is less in the case of that produced at 130°C. This apparent anomaly may be explained by the differences in the structures of gelatin gel and hides and skins. In the latter case, capillary action helps penetration, while in the gel, concentration gradient and molecular size play the main part. In other words, diffusion velocity is directly proportional to the size of particles in the experiments done with gelatin gel. Thus, the maximum penetration in Experiments Nos. 3 & 6 of Table III is due to the maximum average molecular weights of the tanning materials, which do not guarantee a maximum capillary action. This is quite in agreement with the above facts and has also been confirmed practically by tanning skin pieces with the different materials. It was noted in the experimental pieces that the one tanned by the material obtained at 100°C was struck through in the least time, while the time taken in the case of condensate (F) of Table I, was maximum.

The data in respect of the effects of pH on fixation (vide Table V) indicate that the maximum fixation is ensured by adjusting the pH of the tan-liquor to 2.5. The fixation is least at pH 5, i.e., in the isoelectric range (pH 4.7) of the hides and skins. It is evident that the fixation is dependent on the degree of swelling of the hide protein, since the swelling is maximum at pH 2.5 and minimum at the isoelectric point. This may be explained by assuming that up to a certain limit the increased swelling of the pelt is accompanied by a corresponding increase in the diameter of the capillaries in the hide, so that greater amounts of tannins can diffuse through them. As the swelling also increases above the isoelectric point, the increased fixation at pH 6 is consistent with the above view. It may be noted that this behaviour of the Lignosulphonate-Resorcinol condensate is similar to that of the vegetable tannins.

In order to ascertain an optimum pH for penetration, Experiment No. 6 was performed, which leads to the conclusion that the penetration is quickened by adjusting the pH of the tan-solution at relatively high values *e.g.* ' 6 '.

The study of the effect of concentration of the tanning material on its fixation to the hide protein (Table VII) further suggests that penetration is a function of concentration gradient. While a hide or skin lies in a tan-liquor, the concentration of Tannins in solution, both outside and inside the hide or skin have a tendency to reach an equilibrium, and this behaviour of Tannins results in the progress of penetration and finally their fixation from the concentrated solutions. According to the observations listed in Table VII, the increase in concentration of the tan-liquor from 1.8% to 3.3% tends to raise the value of fixation only by 3%, while a further increase from 3.3% to 4.3% results in the increase of fixation by 8.6%. Again, further increase in the concentration of the solution from 4.3% to 8.6% does not show an appreciable rise in degree of tannage for every change of concentration by 1%. However, a maximum amount of fixation is obtained from a 8% solution of the tanning material. In this way, it is established that the maximum degree of tannage is attained at a concentration of 4% or 8%.

Conclusion.

Whereas a magnesium Lignosulphonate Resorcinol condensate was found to be insoluble by previous workers, the sodium salt of Lignin Sulphonic acid condenses with Resorcinol at 130°C giving a soluble product, which can be advantageously used for tanning hides and skins in the manner described below :—

Delimed or depickled goat skins are handled or 'drummed in a 15°Bk solution of the tanning material at pH 6, when a quick penetration is effected. More of tanning material is added from time to time to maintain the concentration of the tan-liquor near about 15°Bk. After complete penetration, the concentration of the liquor is gradually increased to 30°Bk and the pH brought down to 2.8—3. The pelt is then left overnight in the solution. Next day it is lightly washed, slicked out, oiled and dried in a shady place. It is advisable to stake the leather while it is still in the sammed condition. A leather of good feel and strength is thus obtained. The colour of the leather which is rather dark may, however be improved in a number of ways commonly practised in the trade *e.g.*, by slightly myrabing it, or by bleaching with a syntan. Brushing the final leather with a dilute solution of Borax and Oxalic acid also improves the colour.

Treatment of the Lignin Sulphonate-Resorcinol Condensate with Hydrosulphite was also found to improve the colour of the leather considerably. This is being further investigated in the laboratory and the results will be published elsewhere later on.

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Director's Laboratory,
Dated 29th June, 1956.

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CLASSIFIED ABSTRACTS

RAW MATERIALS

IMPROVED HIDE CURING PRACTICES—*F.L. De Benkelaer. Lea. Manfr.* **73**, *2, 29, 1956*).

The improved brine curing process of hides in meat packing industry of America differs from the conventional methods in that the cheap labour rate permits use of more manual operations and also keeps hides in pack for long periods in cellars under controlled conditions of temperature and humidity. The equipment used has a capacity for 25,000 pounds of green hides and five-time this weight of saturated brine solution. The motor driven paddles mounted diagonally opposite, rotating in the same direction, exposes the entire flesh side to the action of brine and also keeps the composition of brine uniform. An additional feature comprises of a centrifugal pump to circulate the brine from the vat through a salt restrengthening box, to maintain the saturation level. The minimum bringing period is from 15 to 16 hours and the temperature of brine varies with the season but is usually 60 to 70°F. The loading and unloading of hides is done by means of a mechanical device. Brine cured hides are superior in that

1. The cure is faster, more uniform and affords greater protection whenever the product is subjected to adverse conditions during shipping or subsequent storage.

2. This cure practically eliminates the development of socalled "salt stains" even on prolonged storage.

3. These hides require no washing before "soaking back" at the tannery and permit the latter operations to be significantly shortened.

4. The leather produced from brine cured hides is plumper and has a clearer grain.

5. These are resistant to attack by bacterial contamination.

N. S.

SEPARATION OF EPIDERMIS FROM DERMIS BY FILTRATES OF TRICHOPHYTON MENTAGROPHYTES—*Nature* **177**, *4519, 1085, (1956).*

The fungi of trichophyton group which are pathogenic and cause skin deseases liberate proteolytic enzyme or enzymes at the site of infection. It is believed that the fungi just grow on the superficial layer of epidermis and proteolytic enzymes diffuse from it and loosen the epidermal attachments. The presence of protease in the skin causes itching and rubbing at the site of infection and this along the loosen epidermal attachment usually make vesicles to appear at the infected spot. This leads to produce damaged skins and hides due to fungal infection.

TANNING

Chrome Tanning

A COMPARISON OF LEATHER PRODUCED BY REGULAR SUGAR REDUCED CHROME LIQUORS AND HIGH BASIC SO_2 REDUCED CHROME LIQUORS AND THE EFFECT OF CHROME LIQUOR BASICITY ON CALF LEATHER QUALITIES—*Robert Stubbings. The Lea. Manfr.* **73**, *2, 40, (1956).*

A detailed study has been made at the Lehigh Laboratory on the successful use of SO_2 reduced chrome liquors and the effect of basicity on leather properties since leather tanned with SO_2 reduced liquors were not as full as those from regular sugar liquors. This was due to the low basicity of SO_2 reduced liquor and any adjustment was not found to produce the same effect as built in basicity. It was found that liquors upto 50% basic could be produced by starting reduction with SO_2 until about 1/3 complete and then by addition of Na_2SO_3. Preparation of liquor was further simplified by using caustic instead of Na_2SO_3 and complete reduction with SO_2 to get 45% basic liquor. Practical tanning trials and evaluation after finishing revealed that leathers-tannel with SO_2 liquor were equal in quality and also produced a fuller leather than the regular sugar liquor. It is to be investigated whether this SO_2 liquor can be effectively used on chrome resin retanned leather or chrome heavy vegetable tanned leather. A study of the chrome liquor basicity was made to determine the qualities of calf leather and the results indicated that

(1) Very low basicity (30%) tends to give poorer break, less roundness and firmer leather than all higher basicities.

(2) Medium low basicity (35%) tends to give less roundness, and firmer leather than higher basicities.

(3) Increase in basicity generally produces softer leather.

(4) Basicity has practically no effect on grain smoothness.

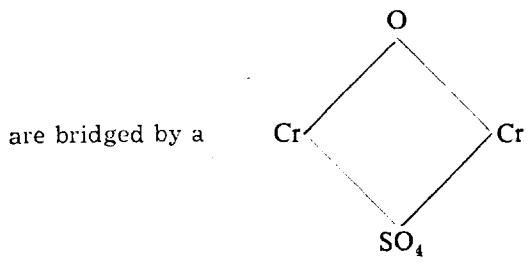
(5) Basicities between 40% and 50% generally produce about same quality leather except that high basicity tends to be softer.

N. S.

TANNING OF GELATIN BY CHROME ALUM. II. FIXATION OF CHROMIUM ON GELATIN—*A.M. Venet—Bull. Soc. Chim. France,* 1955, 1336. *Via. Chem. Abst.,* 1956, 50, 4537. *Via. Brit. Gel. & Glue Res. Assn.* 7, 2, 12, (1956).

Gelatin solution of varying concentrations were treated with chrome alum solutions adjusted with sulphuric acid or sodium hydroxide to various pH values upto 5, for 24 hours, during which the pH was frequently adjusted. The tanned gelatin was precipitated by pouring into 95% ethyl alcohol, filtered, washed with 50% aqueous ethyl alcohol to remove free salts, and dried at 100°C. Samples were analysed for fixed chromium. The plots of fixed chromium versus residual chromium seemed to approach a limiting value, which however, was not reached because too strongly tanned gelatin formed rigid gels difficult to handle. The amounts of chromium fixed were independent of gelatin concentration and increased with pH. Values of sulphate ions fixed were corrected by substracting

the amounts fixed at the same pH from alkali sulphate solutions of the same concentration. At pH 2.5-5, one sulphate ion was fixed per two chromium fixed ; at lower pH, more sulphate ion was fixed ; this may be due to hydrolysis of gelatin exposing more amino groups. It is suggested that at pH 2.5-3.25 two carboxyl groups of gelatin



are bridged by a Group.

Vegetable Tanning

A CORRELATION OF TANNIN CONTENT WITH TANNIN-FORMALDEHYDE PRECIPITATE—*F.R. Humphreys. J.S.L.T.C.* **40**, 5, 147, (1956).

A linear regression has been shown to exist between the tannin content of *Pinus radiata* bark and the tannin/formaldehyde percentage, thereby enabling an estimate to be made of the former from experimentally determined values of the latter. An expression has been calculated for this purpose.

TAN BARK EUCALYPTS OF THE SEMI-ARID REGIONS OF S.W. AUSTRALIA—G. E. *Brockway and W. E. Hills. Emp. Forestry Rev.* 1955, 34, 21. *Via. J.S.L.T.C.* **40**, 5, 179, (1956).

Seven tannin bearing eucalypts are described ; these include the "mallets". The bark of the brown mallet (*E. astringens*) contains 40-50% tannin ; the wood of this tree being more valuable than that of wattle, it is recommended for afforestation.

Processes after Tanning

PROTEIN TYPE FINISHES—*Anthony J. Pilar Jr. The Lea. Manfr.* **73**, 3, 18, (1956).

The practical use of protein type materials such as casein, albumin etc. in the leather finishing is described. Protein type finishes have long shelf-life. They withstand extreme temperature changes and can be mixed with a large variety of materials in almost any ratio with little fear of coagulation or precipitation. They are water soluble and the equipment used can be cleaned easily. These finishes are non-inflammable and non-alergic and also retain the porosity of the leather after finishing. They also preserve the natural high quality found in the most expensive leather products ; and also possess the abrasion or water resistance.

K. S. R.

RESIN EMULSIONS AND WATER TOP FINISHES—*Louis E. Stahl. The Lea. Manfr.* **73**, 2, 12, (1956).

The emergence of colour to meet fashion modes and the several developments that took place in the shoe and leather industries since the war necessitated the requirement of waterproofness and greater degree of scuff resistance most important in finishing upper leather finishes. The addition of polymerized type of resin emulsions such as acrylics, vinyl acetate etc. had come into light. Though waterproofness was improved, these emulsions gave plastic look to the leather and presented problems in plating, swabbing and spraying. It was found that only small quantity of resin emulsion could be used in casein top finishes to get the required properties. The proper application and appearance of the top finish is found to be dependent on the fineness of the particle size of the emulsion. With the outcome of the emulsion polymers of extremely fine particles and with proper selection of starting monomers to give the desired functional properties, it is now possible to make top finishes consisting chiefly of resin to meet the requirements of the shoe industry. These new materials impart permanent flexibility, superior pull over and lasting properties. Their compatibility with all ingredients used in leather finishing and their superior pigment binding properties can be of great advantage in leathers that require coverage. The hazards involved in the use of inflammable materials and the problem of combustibility of residue are eliminated.

K. S. R.

THEORIES

STRUCTURE OF COLLAGEN—*Nature*, **177**, 4511, 710, (1956).

The coiled-coil structure for collagen, earlier put forward by the author [Nature, **176**, 501 (1955)] has been discussed in the light of criticisms made against it. It has been contended that although a triple-chain non-coiled coil structure might be found in some polypeptides and elastin, for collagen, the structure obtained by rotating the minor helices about their own axes through a negative angle (minus configuration) is to be preferred. The reasons for the preference of this structure are that (i) the fly-pro-hypo sequence can occur in this structure without strain, thus having glycine as the every third resides ; (ii) the hydroxyl group of hydroxyproline may be linked to the carboxyl oxygen of another set of triple-chain, which is confirmed from the wide-angle pattern of tanned collagen ; (iii) the distance between the different sets of triple-chains are of the same value as found for dry collagen ; (iv) its Fourier transform agrees better with experiments. The difficulty regarding the formation of more than one hydrogen bond per three residues in a chain is said to be partially removed by not strictly adhering to the coiled-coil structure, and/or by assuming the inter-chain imino-carboxyl linkage through firmly bound water.

G. R. C.

TESTING

SIGNIFICANCE OF pH IN LEATHER MANUFACTURE—*P. Kollar. The Lea. Tr. Rev.* **119**, 3651, 385, (1956).

It is a well known fact that the pH value plays a decisive part in the various stages of leather manufacture. Theory of swelling and the theory of charges on the leather surfaces are dependent on the function of pH. As collagen forms 98 p.c. of the dry matter of the corium the latter is influenced by pH. The most obvious change occuring in the corium is swelling below pH 4.5 and above pH 9 while there is practically no swelling at all over the range pH 4.5. The beamhouse operations are influenced by pH, the optimum ranges of pH being, for soaking 12.5, for bating 7.5 to 8.5 and for deliming 6.5. In respect of particle size of tannins in vegetable tanning, the state of dispersion of the dissolved and undissolved constituents is influenced by pH of the system as well as its concentration and temperature. Particle size of the tannin increases as the pH increases from pH 2 to pH 5 and diminishes as the pH increases from pH 5 to pH 8. The intensity of tannage increases between pH 2 and pH 5 whereas it decreases between pH 5 and pH 8. These findings enable vegetable tanning process to be controlled by artificial acidification of tan-liquors. The recent developments are, the pH control of the raw materials to be used and of leathers, the determination of the differential figure i.e. measurement of pH of solutions or of leather extracts to avoid acid damage to leathers, the pH measurement of wet leathers and in plotting the potentiometric titration curve of deliming agents for assessing their deliming effect or of tan-liquors for adjustment to the required pH value.

K. S. R.

POLAROGRAPHIC INVESTIGATION OF FUR DYES AND THEIR OXIDATION PRODUCTS—*G. Sandberg. J.S.D.C.* **72**, 5, 227, (1956).

The effect of pH on the oxidation of p-phenylenediamine has been investigated. It has been found that the maximum yield of one of the oxidation products—benzoquinone-1:4-bis-(2:5-diaminoanil)—is obtained in a pH interval at which acidity has a marked effect on the state of aggregation of this compound. A change of pH from 6.0 to 7.3 causes its diffusion coefficient to change from $4.8\times10-^{6}$ to $1.0\times10-^{6}$ sq. cm./sec.

As this pH interval covers that used in technical fur dyeing, even small fluctuations in pH have an intricate effect on the diffusion properties of this oxidation product, and therefore also on fur dyeing. Absorption spectroscopy indicates qualitative differences between oxidation products formed at different pH values. There is equivalence between the shifts of position and changes of shape of the absorption bands and the observed changes in slope of the curves of half-wave potential against pH for the different products.

Catalase in the presence of hydrogen peroxide accelerates the oxidative condensation of benzoquinone-1:4-bis-(2:5-diaminoanil). This change can thus be effected very rapidly without applying the usual chromium or copper salts.

Some applications of vertical paper electrophoresis are given, including separation and identification of oxidation products formed under different conditions, and also demonstration of differences between the dissociation constants of different nitro derivatives.

Besides the use of the analytical results in determining the percentages of p-phenylenediamine and related compounds in batches from different suppliers, polarography provides a valuable means of determining exhaustion curves in dyebaths, usually comprising a mixture of five or six oxidisable, reducible, and non-reducible substances, where colorimetric methods would meet with difficulties. Hydrogen peroxide, which is always present, is eliminated by the addition of catalase to the different samples of dye liquor.

POLAROGRAPHIC BEHAVIOUR OF SOME ELEMENTS IN CONCENTRATED CALCIUM CHLORIDE SOLUTION. V. DETERMINATION OF CHROMIUM IN THE PRESENCE OF NICKEL—*J. S. Beveridge, G. F. Reynolds and H. I. Shalgosky. Anal. Chim. Acta* 1955, 13 (5), 494-498. *Via. Anal. Abst.* 3, 5, 1336, (1956).

An extension of previous studies (Anal. Abstr. 1954, 1, 27, 28 and 1210) on the polarography of Ni and Cr in conc. aq. $CaCl^2$ at pH $\geqslant$ 3.5 and temp. of 90° to 100°C is reported. For the direct determination of Ni and Cr when present together (*e.g.*, in calcium metal), the combined Ni and Cr wave is obtained first in 5 M $CaCl_2$, as described previously. The Cr wave only can then be obtained in a $CaCl_2$-hydroxylamine base electrolyte (adjusted to 7.4 M Cl′ and 0.4 M NH_2OH) and the concn. of Ni and Cr can be calculated from calibration graphs. The concn. of each metal should preferably be from 6 to 60 μ g per ml, with Ni:Cr $\geqslant$ 2.

THE REACTION OF CHROME COMPLEX COMPOUNDS WITH ION-EXCHANGE RESIN. III. EXCHANGE REACTIONS BETWEEN A CATIONIC EXCHANGER OF STYRENE TYPE AND CATIONIC COMPLEX IONS OF CHROMIUM—*Yoshiyuki Inoue, Akira Kawamura, Keizo Wada and Hroshi Okamura. Japan Analyst,* 1955, 4(5), 277-280. *Via. Anal. Abst.* 3, 5, 1337, (1956).

The ion-exchange reaction between $[Cr(H_2O)_6]\ldots$ and $[Cr(H_2O)_4(Ox)_2]$· (Ox=oxalate) and Amberlite IR-120 was studied in various salt forms of the resin and it was found that the exchange proceeds well when the resin is in the form of hydrogen, sodium and potassium salts. It was also found that the size of the network structure of the resin has a significant effect on the exchange with chromium complexes. Sulphonated polystyrene (I) exchanges with Cr complexes better than the usual IR-120 or 112, which contain a significant amount of divinylbenzene and thus have a smaller network structure. I also exchanges well with a soln. of cationic chromium complexes which has been subjected to partial hydrolysis or treatment with alkali.

IV. SYSTEMATIC ANALYSIS OF COMPLEX IONS OF CHROMIUM WITH SULPHONATED POLYSTYRENE AND AMBERLITE IR-4B—*Ibid.*, 1955,) (5), 281-285. *Via. Anal. Abst.* 3, 5, (1956).

A systematic separation of complex ions of Cr with various charges was studied with an ion-exchange resin. A mixed solution of chromium

complexes with different charges is passed through a column of I. Both the tervalent and univalent cationic complexes exchange quant. with I. Neither the tervalent nor non-electrolytic complex is absorbed on I, but a significant amount of univalent anionic complex is absorbed. The elute is passed through a column of Amberlite IR-4B (acetate). Both uni- and ter-valent anionic complexes are quant. exchanged and only the non-electrolytic complex is found in the eluate. Both cationic and anionic univalent complexes on the column of I are eluted with 0.05 N $HClO_4$, whereas the tervalent cationic complex remains on the column and is eluted on the passage of $>$ 20 ml of N $HClO_4$ (for 15 mg of Cr). By passing the 0.05 N $HClO_4$ soln. through a column of IR-4B, the univalent anionic complex is adsorbed on the column and the univalent cationic complex is found in the elute. The amount of Cr is determined in each fraction to give the amounts of complexes on different charges. This method can be applied to the study of ageing of chromium complexes including Cr tanned materials obtained by the reduction of $K_2Cr_2O_7$ with various reducing agents.

THE IDENTIFICATION OF VAT DYES—*D.A. Derrett-Smith and J. Gray. J.S.D.C.* **72**, 5, 211, (1956).

The tables published in 1940 by Derrett-Smith and Bradley and in 1947 by Derrett-Smith and Gee have been brought up to date to include all the British, German and Swiss vat and solubilised vat dyes which have appeared on the British market since 1940. Dyes which were included in the original tables but have since been made by other firms are included under their new names.

In addition, it is shown that certain vat dyes behave differently when treated with sodium hydrosulphite and sodium hydroxide as compared with sodium hydrosulphite and sodium carbonate.

A DIRECT MICRO-ALKALIMETRIC TITRATION METHOD FOR DETERMINING SULPHUR IN ORGANIC COMPOUNDS—*J. Smith and A. C. Syme. The Analyst* **81**, 962, 302, (1956).

A direct micro-alkalimetric titration method for determining sulphur in organic compounds containing nitrogen and chlorine is described. The method is applicable both to wet and dry-combustion methods, the ultimate product, barium sulphate, being treated with an ion-exchange resin, and the liberated acid titrated.

BYE-PRODUCTS

GELATINE PAD FOR POTTERY PRINTING—*W. Harrison. Pott. Gaz.*, 1955, **80**, 1053, *Via. Ceram. Abs.* 1955, 2870. *Via. Brit. Gel. & Glue, Res. Assn.* **7**, 2, 7, (1956).

Some of the earlier uses of the gelatine pad in the pottery industry for printing purposes are outlined and problems to be overcome for modern applications discussed. The paper-transfer process is briefly discussed. Attention is paid to the machine patented by Rowe in 1903:

a resilient pad was brought down precisely in position on a lithographic stone or the like. Rowe used a rubber pad, which can be successful with a properly selected range of colours.

GENERAL

CAPILLARY SPACES AND FIBRE SURFACES IN LEATHER—*R. G. Mitton. Lea. Tr. Rev.* **120**, 3652, 25, (1956).

The comparative measurement of the volume of the capillary spaces in a leather infers that certain liquids and gases do not penetrate extensively into the molecular structure of the fibres although water and some polar molecules do so. The area of the surface of the fibres can be measured either by measuring the quantity of gas that can flow through the leather structure under specified conditions or by measuring the amount of gas absorbed or condensed on the fibre surfaces when they are cooled to low temperature and exposed to the gas. Both methods indicate that, in dry leather, one grain of leather has an area of the order of one sq. metre. Leather fibres swell when they absorb moisture from damp air and their volume increased by about 25 per cent. The swollen fibres are more easily stretched longitudinally than dry fibres but they are found to be weaker than the latter. But the moist pieces are found to be stronger than dry because the fibres in the former can better align themselves to resist a pull imposed on the piece. The rate of penetration of tans is slower than water but the former modify the extensibility and other properties of the fibres. Oils and fats added to leather appear to remain entirely on the fibre surface or between the fibres, when they act as lubricating agents rather than as components of the fibres themselves. The capillary spaces and fibre surfaces in hides and leather are thus important because properties of the finished leather are dependent on its fibre structure.

K. S. R.

THE ECONOMIC IMPORTANCE OF TANNERY ORGANISATION—*L.H.G. Kortright. Lea. Manfr.* **73**, 2, 25, (1956).

The author has reviewed his experiences to stress the importance of the systematic work run on the principles of factory organisation in tanneries. Organisation in an industry springs progress and achieves the maintenance of quality standards of the goods produced at the lowest cost. Details about the personnel, production planning, manufacturing, technical control and research, equipment maintenance, power supply and purchasing sections of the production division of his company, are given.

K. S. R.

THE PRESERVATION OF BACTERIA—*R.I.N. Greaves. Can. J. Microbiology* **2**, 3, 365, (1956).

The method of centrifugal vacuum freezing together with the use of a drying medium consisting of three parts serum one part broth, and 7½% glucose has been shown to be suitable for preserving bacteria in the dry state. The method, however, demands a very rapid speed of evaporation and this may lead to contamination of the apparatus and even cross-contamination of cultures. Also, since the temperature of drying is not very low the choice of drying medium is restricted because of the frothing of many media that would otherwise be suitable. To overcome these difficulties an apparatus was designed for drying at a temperature below -30°C. With this apparatus a highly effective drying medium containing no protein can be used. The drying medium recommended for use with this apparatus consists of equal parts of 10% dextran and 12% peptone to which is added glucose 7½% (w/v) and a detergent "Triton W.R. 1339", 1/4000 (w/v).

PATENTS

BATING WITH THIOGLYCOLLIC ACID—*Osterreichische Stickstoffwerke. Fr. Pat.* 1,097,131 ; *Rev. tech. industr. Cuir,* 1955, 47, 211. *Via. J.L.T.C.* **40**, 5, 179, (1956).

Pancreatic enzymes are liable to attack collagen. It has been found that acids or their salts derived from mercaptans, such as thioglycollic acid, will remove globular proteins without attacking the collagen. In general, 0.5-3% of the substance (on weight of skin) is used ; less is required if the acid is used. The material is applied at normal, or slightly elevated, temperatures. Thioglycollic acid or its salts may also be added to soak liquors or lime liquors, but in these cases a reduced quantity is used.

ADJUSTMENT OF pH AND SALT CONTENT OF VEGETABLE TAN LIQUORS BY ION-EXCHANGE RESINS—*Toten Cellulosefabrik. Brit. Pxt.* 739, 312, 1955. *Via. J.S.L.T.C.* **40**, 5, 179, (1956).

To maintain a low pH in vegetable tan liquors, and to avoid the increase in salt content caused by the addition of strong acid, part of the liquor in process is led to a settling pit, when it is pumped through an acid cation exchanger back to the process system .The method is particularly applicable to systems employing sulphite cellulose liquors.

BOOK NOTICES

WATTLE TANNING AND MIMOSA EXTRACT—*By the Leather Industries Research Institute, Grahamstown, S. Africa.* 1955. *Pp.* 205. *Price* 41/-. *Via. J.S.L.T.C.* **40**, 5, 179, (1956).

This publication is described as a report drawn up to provide information for tanners and tannery chemists, and replaces a book issued by this Research Institute some ten years ago under the title of "The properties and practical application of wattle tannin".

The subject matter is divided into three parts, the first of which provides an historical background, an outline of the process of mimosa extract manufacture and the functions of Wattle Research Institute and the Leather Industries Research Institute in relation to the South African Wattle Industry. Part 2, is essentially theoretical, and describes work done at Grahamstown and elsewhere on the composition of mimosa

extract, molecular weight studies, astringency factors, penetrating properties, bisulphiting and a comparison of extracts from various Acacia species. Part 3 concerns the more practical aspects of the subject and includes chapters on a comparative survey of tanning properties, analytical control of mimosa liquors, colour control and sludge formation, bleaching of mimosa extract, production of a sumac substitute, and mimosa tannages of heavy and light leathers. This last chapter will be of particular interest to the tanner as it includes details of rapid mimosa tannages based on simple pH control.

Much of the original work referred to throughout the book has appeared in this Journal, and may be familiar to many readers. At the same time, however, it is a definite advantage to have the information in one volume, and written by those responsible for the original researches. This, supplemented by references to other investigations in the same and allied fields has resulted in a publication which should have a wide appeal in the industry.

SYNTHETIC ION-EXCHANGERS—*Recent developments in theory and Application. G.H. Osborn, F.R.I.C. London : Chapman & Hall Ltd.,* 1955. *Pp.* 191. *Price* 30/- *cent. Via. J.S.L.T.C.* **40**, 5, 180, (1956).

This book is notable for containing the most complete bibliography of papers on ion exchange that has yet been published. The bibliography is conveniently divided into applications of ion exchange and theoretical papers on structure and fundamental properties of these valuable materials. The preceding chapters give a brief but good account of the structure of the new types of resins and their equilibrium properties. A very useful chapter gives descriptive matter of the commercially available resins made in the U.S.A. and this country. The book is up-to-date, and has chapters on the novel process of ion exclusion and the use of ion exchange membranes. The author rightly describes his contributions to the analytical uses of ion exchange, and the book as a whole can be recommended as a useful addition to the small library on ion exchange.

GERBEREICHEMISCHES TASCHENBUCH—*By Dr. A. Kuntzel. Sixth Edition. Verlag von Theodor Steinkopff. Dresden and Leipzig,* 1955. *Pp.* 319. *Price* 34/- *net. Via. J.S.L.T.C.* **40**, 5, 180, (1956).

This is a completely revised edition of what was formerly known as the VAGDA handbook, written by Prof. E. Stiasny while at Darmstadt. At the hands of its new author, Dr. A. Muntzel, it has been considerably enlarged to include some recently introduced techniques. Thus the use of complexone (sequestric acid) for determining calcium and magnesium hardness is referred to in water analysis, and masking agents are included in the section on chrome liquors, to mention just two additions.

The whole range of materials used in leather production is included, and a useful collection of analytical methods has been brought within the compass of a convenient sized laboratory manual. For the examination of tanning materials, pride of place is given to the filterbell method with references given to the shake method and its sveral modifications. This,

however, must be expected in a laboratory book designed particularly for the continental user. The Procter-Searle method for acidity in vegetable tanned leather is now omitted, and pH measurements only used for this determination. Physical tests for leather are dealt with in some 28 pages, rather brief, admittedly, but again it must be remembered that the work has no pretentions at being an exhaustive treatise, and the reader will find the references to original work most useful when some particular determination requires following up. Indeed, throughout the book, references are a feature, adding greatly to its usefulness, and Dr. Kuntzel should be complimented on adding such a volume to our present meagre selection of leather trade literature.

NOTES AND NEWS

BAVONIZED LEATHER.

Bavon 66 is partially neutralised alkenyl succinic acid which contains two potentially reactive carboxyl groups. It is hydrophobic in nature and is used to impart waterproofness to shoe leather. The Bavon process is applicable to most type of side leathers. The material can be applied from grain or flesh side. The advantages of Bavonized leather are that they are water resistant, economical to produce, softer and stays soft, permiable to moisture vapor and moisture absorbent on the flesh side.

—*The Lea. Manfr.* 73, 2, 37, (1956).

NEW SYLFLEX PROCESS PRODUCES LEATHER RESISTANT TO MOISTURE.

The property of water-repellency in leather is obtained by the use of silicone. A special silicone with the trade name Sylflex has been developed by Dow Corning Silicones Ltd. The claims of Sylflex tanned leather is that not only the property of water-repellency is incorporated, but also retains the other characteristics of leather. Like ordinary leather, sylflex tanned one has got the breathing capacity. "It keeps water out —lets air in." This property of resistance to moisture also ensures the leather to be resistant to damage from acids, perspiration, etc.

—*Shoe & Leather Journal,* **69**, 5, 62, (1956).

A NEW CELLULOSE CEMENT.

Nitrocellulose cements, often designated pyroxylin or cellulose, have, of course, been used for leather sole-bonding in the adhesive method of shoe making since the introduction of the original "stuck-on process" several decades ago. These cements have many advantages from the point of view of both the shoe manufacturer and shoe repairer which the more modern cements made from synthetic materials do not possess.

The chief of these advantages are comparative ease of application and reliability in wear. A nitrocellulose bond will stand up to all reasonable conditions met with in wear, and especially in tropical climates, for it remains unaffected by oil or grease, moisture, or heat. Hitherto one of the chief disadvantages of this cement, however, has been that the cemented sole, after activation, cannot be "spotted" to the shoe and the

operator has to hold the sole firmly in place until pressure has been fully applied to avoid slipping. Consequently production is slowed down.

This difficulty has been overcome by the introduction by Vik Supplies Ltd., Stafford, of an entirely new nitrocellulose cement, Vikstik No. 901. This cement has all the good characteristics of the older types of nitrocellulose cement with the additional property of instantaneous "tack" after activation. Additional features of Vikstik No. 901 are that it has a greater bond strength, has a greater flexibility of bond, and a slightly increased penetrating power into "difficult" upper leathers. Tested on the Satra machine most nitrocellulose cement bonds, such as that of Vikstik No. 108, will break at 25-30 lb., but with Vikstik No. 901 this is increased to 50-60 lb.

In all other respects—application, drying and other working characteristics—the new cement is the same as the older types. Pre-cemented soles can be stored almost indefinitely, and the surfaces can be activated prior to attachment by solvent dipping, using the Lotus Activating and Conforming Unit, or by the use of a bodied softener brush or machine applied.

The new cement should be of particular interest to repairers especially those whose preference continues to be for a nitrocellulose adhesive. It will obviate the need for using rivets to secure the sole in its correct position while the cement dries. The time the work needs to be kept under pressure is reduced considerably—five minutes being generally sufficient—and providing the two surfaces are brought together after a drying time of ten minutes the use of a solvent is not necessary.

When the cemented surfaces are allowed to dry for longer than 10 minutes one of them needs to be activated with a solvent.

Bodied solvents graded to accelerate or delay the drying time are obtainable, but for general use by repairers Vikstik No. 217 Bodied Softener is most suitable.

Vikstik No. 901 is a true nitrocellulose cement and, like all others, it cannot be heat-activated.

—*Shoe & Lea. News,* **149**, 2093, 95, (1956).

EAST INDIA TANNED HIDES AND SKINS FOR INTERNATIONAL FAIR.

Representative samples of the principal products of the South Indian tanning industry have been sent from Madras to Germany for display at the ensuing International Fair to be held at Frankfurt and Zogreb.

The samples which consist of E. I. tanned kips, goat and sheep skins, box and willow leathers, glace kids and reptile skins, were collected from various tanneries of South India by Mr. E. C. Sankar, Deputy Chief Controller of Imports and Exports, Prof. B. M. Das, Director of Central Leather Research Institute and Mr. Jamal Mohideen, representative of the tanning industry.

It may be mentioned that there is a very large demand for E.I. tanned kips and skins in England, U.S.A. and Japan. German leather

dressers and manufacturers are also keenly interested in Indian leathers. It is stated, England is now the centre of distribution and the German leather goods manufacturers generally make their purchases from the London auctions which are periodically held to sell Madras tanned leather. The display of these leathers in the International Fair, it is felt, will help to arouse the interest of the German consumers in these goods and make them deal with India directly.

STANDARDS FOR LEATHER.

The Leather Sectional Committee of the Indian Standards Institution has decided to adopt statistical methods in prescribing sampling procedures.

The Committee, which concluded a two-day meeting here under the chairmanship of Prof. B. M. Das, Director of the Central Leather Research Institute, Madras, also finalised standards for russet and chamois leather, and draft standard methods of sampling and test for oil tannel leather.

The meeting was attended by representatives of manufacturing interests, the Commerce and Industry Ministry, defence laboratories and leather research institutes in India.

—*Indian Express,* dated 28th July, 1956.

C. L. R. I. NEWS

A farewell party was got up on 13th July, 1956 by the staff of the Institute to meet Sri T. K. Vedantachari, on his retirement as the first Administrative Officer of the Institute.

Prof. B. M. Das, the Director, Dr. Y. Nayudamma, the Assistant Director and the representatives of the staff spoke highly of the qualities of Sri Vedantachariar—his quickness of disposal of cases, his sound advice, his manner of conducting himself in his responsible and difficult post, etc., and wished him success in his work of evolving and spreading his system of Hindi shorthand in furthering the national cause of helping the spreading of Hindi. A token present was also given to him.

Sri Vedantachariar suitably acknowledged the good words said of him by giving advice to the staff.

Sri G. R. Venkataraman proposed the vote of thanks.

Exhibits have been sent from the Central Leather Research Institute to the International Industries Fair at Prague, Czechoslovakia, for display.

Prof. B. M. Das, Director, Dr. S. K. Barat, Senior Scientific Officer (Director's Laboratory) and Mr. B. N. Pal, Senior Scientific Officer (I.C.A.R. Scheme), attended a two-day meeting of the Leather Sectional Committee of the Indian Standards Institution held at Calcutta.

Dr. Y. Nayudamma, Assistant Director, delivered the inaugural address of the Chemical Society of the Loyola College on 26th July, 1956.

Dr. Y. Nayudamma, Assistant Director, gave evidence before the Committee of Slaughter Houses and Meat Inspection Practices, that met at Madras, on 27th July, 1956.

Shri T. K. Vedantachari, Administrative Officer, retired with effect from 1st July, 1956.

VISITORS

Name	*Date of Visit*
Mr. R. N. Mohan, Assistant Animal Husbandry Commissioner, Indian Council of Agricultural Research, New Delhi	27-7-1956
Mr. Berti A. D'soza, Principal, Veterinary College, Madras	27-7-1956
Mr. I. D. Mantramurti, Deputy Director of Animal Husbandry (Veterinary), Madras	27-7-1956
Mr. F. D. Wilson, Lecturer, Madras Veterinary College, Madras	27-7-1956
Mr. Raymond H. Ewell, Chemical Economist, Stanford Research Institute, now attached to the Ministry of Commerce & Industry, Govt. of India	1-8-1956
Mr. V. Ganapathi, Assistant Director, Small Industries Service Institute, Madras-6	1-8-1956
Mr. Ranbir Kishore, Scientific Officer, National Archives of India, New Delhi	7-8-1956

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எழும்பூர், சென்னை-600 008.

தவணைத்தாள்.

சே. எண் : ப. எண் :

வழங்கிய நாள். (1)	திரும்பிய நாள். (2)	வழங்கிய நாள். (1)	திரும்பிய நாள். (2)

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